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Applicants: William E. FORD et al.

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For: SOLUBLE CARBON NANOTUBES

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Respectfully submitted,

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Soluble carbon nanotubes

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Soluble carbon nanotubes

Carbon nanotubes (CNTs) have recently attracted considerable attention due to their unique electronic, mechanical and-structural properties. Carbon nanotubes have been shown to be electrically conducting at the same time as having high tensile strength and elasticity, the ability to absorb gas molecules as nanocapillaries, the potential of further chemical functionalization, and chemical and thermostability. These qualities make carbon nanotubes prime candidates for use in nanomolecular and/or electronic devices.

Carbon nanotubes can be synthesized by a range of methods of which involve the vaporization of elementary carbon by various means. The first synthesis reported took place by the discharge of an electric arc of graphite in the presence of metal catalysts (e. g. Fe, Co, Ni). Alternative routes are based on the laser vaporization of graphite-Ni-Co-mixtures or chemical vapor deposition wherein various carbon sources can be used. At present milligram to gram quantities can currently be manufactured by using such routes, within a matter of hours. The material, thus produced, however, has a substantial amount of contaminants and, in addition, side-wall defects. Carbon nanotubes which result directly from such synthesis methods, without having been further modified, are commonly referred to as "as-prepared carbon nanotubes". In order to remove the contaminants, mainly oxidative treatments have been imployed.

As-prepared carbon nanotubes (CNTs) that are produced in bulk quantities (usually via chemical vapor deposition, electric arc discharge, laser ablation (also known as pulsed laser vaporization), or gas-phase catalytic growth) are generally contaminated with large amounts of impurities (typically 5-50 wt%). The impurities include amorphous carbon, graphite encapsulated catalytic metal particles, graphitic material, and fullerenes. The most common methods for purifying the CNTs involve either liquid-phase or gas-phase oxidation processes, which may be accompanied by solvent extraction, ultra-sonication, centrifugation, filtration, chromatography, and/or microwave exposure. The liquid-phase oxidation processes generally make use of strong adds (primarily HNO_3, H_2SO_4, and/or HCl), sometimes with additional oxidants (e.g., H_2O_2, $KMnO_4$, etc.). Likewise, gas-phase oxidation is sometimes used in conjunction with liquid-phase add treatment, the latter being necessary for dissolution and removal of metal contaminants. Various reaction parameters such as concentration, temperature,

and time have been employed, some representative examples of which are provided in Table 1.

Table 1. Published methods for purifying single-walled CNTs (processes conducted at room temperature unless otherwise noted; aqueous solutions unless otherwise noted; filtration/rinsing and drying steps am omitted in most cases).

CNT production method	Purification steps	Reference
Electric arc	1. Reflux in H,O, 12 h 2. Extract with toluene 4. Bake in air at 470 °C, 20 min 5. Extract with 6 M HCI	Tohji *et al.* (1997)[1]
Laser ablation	1. Extract with CS_2 2. Sonicate in 0.1% surfactant solution, 2 h 4. Microfiltration (3 cycles) 5. Soak in ethanol (to remove surfactant)	Bandow *et al.* (1997)[2]
Laser ablation	1. Reflux in concentrated HNO_3, 4 h 2. Centrifugation, H_20 wash	Dujardin *et al.* (1998)[3]
Laser ablation	1. Reflux in 2.6 M HNO_3, 45 h 2. Centrifugation, H_20 wash 3. Tangential flow filtration 4. Sonicate in 3:1 H_2S0_4/HNO_3, 24 h 5. Treat with 4:1 H_2S0_4/30% H_20_2 at 70 °C, 0.5 h	Liu *et al.* (1998)[4]
Laser ablation Electric arc	1. Treat with $Cl_2 + H_2O$ at 500 °C, 6 h 2. Sonicate in 1:1 DMF:0.6 M HCI 3. Sonicate in DMF	Zimmerman *et al.* (2000)[5]
Laser ablation	1. Reflux in 20% H_20_2, 12 h 2. Extract with CS_2 and CH_3OH	Tang *et al.* (2000)[6]
Electric arc	1. Bake in air at 300 °C, 24 h 2. Treat with conc. HNO_3 at 60 °C for 12 h 3. Sonicate in ethanol and filter (0.3 pm)	Rao and Govindaraj (2001)[7]
Laser ablation	1. Sonicate in 1:1 HF/HNO_3 +surfactant, 5 h 2. Rinse with 0.01 M NaOH	Chattopadhyay *et al.* (2002)[8]
Electric arc	1. Treat with microwaves (150 W) at 500 °C, 20 min 2. Refluxin4MH<1,6h	Harutyunyan *et al.* (2002)[9]
Electric arc	1. Reflux in 2.8 M HNO_3, 6 h 2. Dry at 100 °C, ≥10h 4. Bake in air at 550 °C, 10 min 5. Bake in vacuum at 1600 °C, 3 h	Kajiura *et al.* (2002)[10]

The more oxidative processes probably result in opening of the ends and enlarging the side-

wall defects. As a result, the ends and surfaces of the CNTs become covered with oxygen-containing groups such as carboxylic acid, ether, phenolic, and quinone groups. Heating in a vacuum to 230-330 °C thermally destroys carboxylic acid groups on single walled CNTs, while heating to 800 °C destroys ether and quinone groups. Rao and Govindaraj subjected their purified CNTs to heat-treatment at 400 °C for 0.5 h to remove acid sites on the surface of the tubes and open them. (Rao et al. (2001) *Proc. Indian Acad. Sci. (Chem. Sci.)* **113,** 375). Cai *et al.* ((2002) Chem. Mater. 14, 4235) found that oxygenated functional groups can be removed from single-walled CNTs by heating at 600-800 °C for 5 h. Thermal annealing in vacuum at 1000-1200 °C is expected to cause the open ends to close to hemifullerene end caps. (Liu et al. (1998) *Science* **280,** 1253.)

At present there is one drawback associated with carbon nanotubes which prevents them from being properly processed and further manipulated, which is that carbon nanotubes, inherently, are largely insoluble in most common solvents.

This intrinsic insolubility arises from strong van der Waals and π-π stacking interactions between individual CNTs, which causes them to orient parallel to one another in close-packed triangular lattice. These structures are referred to as "ropes" or "bundles." CNTs that have been subjected to oxidative treatment may have an even greater tendency to form bundles due to carboxyl related secondary bonding forces. Methods that have been developed for enhancing the solubility of CNTs include cutting them into shorter pieces and functionalization. It should be noted that stable dispersions rather than true solutions of CNTs are obtained by some of these methods.

Cutting or shortening of CNTs can be achieved by either mechanical or chemical means. The mechanical methods used include ultrasonication, ball milling, and abrasion. Liu *et al.* ((1998) *Science* **280,** 1253), combined ultrasonication with chemical "etching" for cutting single-walled CNTs.

Hirsch ((2002) *Angew. Chem. Int. Ed.* **41,** 1853) recently reviewed the functionalization of single walled CNTs. There is special interest in water-soluble CNTs for biological applications.

Functionalization of CNTs can be classified as either covalent or non-covalent. Several cova-

lent processes utilize the carboxylic acid (-COOH) group that is generated during oxidative purification for attaching organic amines or alcohols to the CNTs via amide or ester bond formation, respectively. The organic compounds attached included polymers and dendrons. Metal complexes can be attached to single-walled CNTs by coordinative bonding of the metal center to the oxygenated carbon groups. Other covalent modifications described in the literature include reversible sidewall-alkylation of fluorinated CNTs (Boul et al. (1999) *Chem. Phys. Lett.* **310**, 367), reactions with aryl diazonium compounds (Bahr et al. (2001) *J. Am. Chem. Soc.* **123**, 6536; Bahr et al. (2001) *Chem. Mater.* **13**, 3823; Kooi et al. (2002) *Angew. Chem. Int. Ed.* **41**, 1353), ultrasonically-induced reactions with monochlorobenzene and poly(methyl methacrylate) (Koshio et al. (2001) *Nano Lett.* **1**, 361), addition reactions of nitrenes and nucleophilic carbenes (Holzinger et al. (2001) *Angew. Chem. Int. Ed.*. **40**, 4002), and addition reactions of azomethine ylides (Georgakilas et al. (2002) *J. Am. Chem. Soc.* **124**, 760).

Non-covalent processes for functionalization of CNTs generally involve adsorption of molecules to the sidewalls. Surfactants used for this purpose include sodium dodecyl sulfate (Duesberg et al. (1998) *Appl. Phys. A* **67**, 117; Doom et al. (2002) *J. Am. Chem. Soc.* **124**, 3169) and Triton. The alcohol moiety on Triton surfactants can be used for subsequent covalent chemical modification (Shim et al. (2002) Nano Lett. 2, 285). Polymers can adsorb by a process called "polymer wrapping" (Curran et al. (1998) *Adv. Mater.* **10**, 1091; Tang et al. (1999) *Macromolecules* **32**, 2569; Coleman et al. (2000) *Adv. Mater.* **12**, 213; O'Connell et al. (2001) *Chem. Phys. Lett.* **342**, 265; Bandyopadhyaya et al. (2002) *Nano Lett.* **2**, 25; Star et al. (2002) *Angew. Chem. Int. Ed.* **41**, 2508; Chen et al. (2002) *J. Am. Chem. Soc.* **124**, 9034; Star et al. (2002) *Macromolecules* **35**, 7516). Salt formation between organic amines and the carboxylic acid groups on oxidized CNTs is another non-covalent method for making CNTs soluble (Hamon et al. (1999) *Adv. Mater.* **11**, 834; Chen et al. (2001) *J. Phys. Chem.* **105**, 2525; Chattopadhyay et al. (2002) *J. Am. Chem. Soc.* **124**, 728; Kahn et al. (In press) *Nano Lett*). Lastly, adsorption of pyrene derivatives to the sidewalls of CNTs via π-stacking interactions was used for functionalization. The succinimidyl ester of 1-pyrenebutanoic acid served as a chemically reactive site for forming attaching proteins to the CNTs via amide bond formation (Chen et al. (2001) *J. Am. Chem. Soc.* **123**, 3838).

Despite the above-mentioned cutting and functionalization processes, the carbon nanotubes still exist predominantly in the form of bundles, i. e. agglomerates of carbon nanotubes in

parallel. In the past, several attempts have been made to separate these bundles into single (in the sense "non-bundled") carbon nanotubes via a process referred to as "exfoliation".

Treatment of bundles of single-walled CNTs with 70% nitric acid at 25 °C for 2 hours resulted in an expansion of the inter-nanotube spacing and increase in the amount of hydrogen in the material (Bower et al. (1998) *Chem. Phys. Lett.* **288,** 481). These changes, which could be reversed by heating to 230 °C under vacuum for 12 hours, indicated reversible intercalation of the bundles with HNO_3 molecules. Treatment with the acid for 12 hours resulted in a change in structure and morphology of the CNTs that was not reversed by heating under vacuum. Liu *et al.* ((1998) *Science* **280,** 1253) chose a 3:1 concentrated H_2SO_4:HNO_3 mixture for the oxidizing acid during cutting of CNTs because it was known to intercalate and exfoliate graphite.

Exfoliation is also believed to be a key feature of the mechanical cutting process reported by Chen *et al.* ((2001) *J. Am. Chem. Soc.* **123,** 6201) which involved grinding single-walled CNTs in soft organic materials such as γ- and β-cyclodextrins. According to the authors, the excellent dispersion of the CNTs by the cyclodextrins, together with partial exfoliation, made the grinding forces sufficiently strong to induce local conformational strains on the nanotubes, which eventually resulted in cutting, most likely at their defective sites.

None of the above solubilization attempts and/or exfoliation attempts have been very successful. The methods presently known for this purpose are not easily scaled up to large quantity, they are time-consuming, they still yield solubilized CNTs bundles rather than individual CNTs, and further they require the use of CNTs that have been shortened. Accordingly there is a need in the art for solubilization methods that provide soluble carbon nanotubes capable of dissolving in a variety of solvents, including water. Furthermore there is a need in the art for providing a method of solubilizing carbon nanotubes that have not been shortened and/or include functional groups for subsequent further chemical modification. Also there is a need in the art for a method of solubilizing carbon nanotubes that are applicable to both multi-walled and single-walled carbon nanotubes which methods also allow the production of multi-gram quantities of carbon nanotubes.

All these objects are solved by a method of solubilizing carbon nanotubes comprising the steps:

a) providing, in any order:

carbon nanotubes, and

at least one type of monomer molecules capable of undergoing a polymerization reaction or a precursor of the at least one type of monomer molecules;

b) mixing together the nanotubes with the monomer molecules or their precursor;

c) initiating a polymerization reaction of the monomer molecules

to yield modified carbon nanotubes.

"Solubilizing" is not restricted to a particular kind of solvent. Preferably it means solubilizing in aqueous solution.

In one embodiment the carbon nanotubes have functional groups on their surface and/or ends, wherein, preferably, the functional groups are oxygenated functional groups selected from the group comprising C-O species (alcohol, phenol, ether, epoxide), C=O species (aldehyde, ketone, quinone), and O-C=O species (carboxylic acid, ester, anhydride, lactone).

It is preferred that the carbon nanotubes are single-walled or multi-walled nanotubes.

In one embodiment approximately 1 per approximately 200 to 1 per 10 carbon atoms of the carbon nanotubes, preferably approximately 1 per approximately 150 to 1 per 20 carbon atoms of the carbon nanotubes, more preferably approximately 1 per 100 carbon atoms of the carbon nanotubes are in an oxidized state.

In one embodiment the polymerization occurs at the functional groups.

It is preferred that the monomer molecules are isocyanic acid and/or cyanate ion.

In one embodiment the precursor of the at least one type of monomer molecules is urea and/or its derivatives.

In another embodiment, the precursor of the at least one type of monomer molecules is selected from the group comprising cyanuric acid, cyanuric chloride, isocyanuric acid and trichloroisocyanic acid.

In yet another embodiment, the precursor is a cyanate salt, such as the cyanate salt of an alkali metal or a quaternary ammonium cyanate.

It is preferred that the method according to the present invention comprises the additional step(s):

ba) heating the mixture, or, alternatively,

bb) acidifying the mixture or,

both steps ba) and bb), wherein, preferably the heating and/or acidifying is such, that the precursor of the at least one type of monomer molecules is induced to form said monomer molecules.

Preferably, the at least one type of monomer molecules or the precursor of the at least one type of monomer molecules is provided in a solvent.

In one embodiment the carbon nanotubes are provided in a solvent.

Preferably, the solvent of the monomer or its precursor is the same as the solvent of the carbon nanotubes, or the solvents are different.

In one embodiment, the solvent(s) can be heated to a temperature close to or above the melting point of the monomer or its precursor, without decomposing or evaporating.

In one embodiment, before or after the polymerization reaction, aldehydes are added to the mixture, wherein, preferably, the aldehydes are selected from the group comprising formaldehyde, acetaldehyde, paraformaldehyde, propionaldehyde, benzaldehyde, and glutaraldehyde.

If the aldehyde is added before polymerization, it should have a boiling point greater than approximately 100°C. Paraformaldehyde is a non-volatile polymeric form of formaldehyde that depolymerizes to formaldehyde. Benzaldehyde and glutaraldehyde are common aldehydes with high boiling points (>170°C).

The criterion for the boiling point of the aldehyde in this context, is that the aldehyde can be present during the polymerization without evaporating or decomposing.

In one embodiment, after step c), non-reacted monomer and/or precursor is removed from the reaction, wherein, preferably, the removal occurs by a size separation step and/or an adsorption step and/or by enzymatic degradation, and/or filtration and washing, and/or precipitation, and/or selective burning, and/or plasma treatment and wherein, even more preferably, the size separation occurs by gelfiltration, and the adsorption occurs by gelfiltration, preferably over a dextran-based material, more preferably Sephadex, and the enzymatic degradation occurs by means of urease, and the precipitation occurs by perchlorate, in particular sodium perchlorate. In one embodiment, the precipitation selectively precipitates modified CNTs.

Selective burning is based on the principle that most organics will burn in air under conditions where CNTs are stable. Therefore heating to appropriate temperatures for appropriate times will result in the CNTs remaining while other organics have simply burned away. Reasonable temperature and time ranges are 300°C to 550°C and 10 minutes to 24 hours (shorter times when higher temperatures are used).

Similarly plasma treatment can be used for selective removal of organics on CNTs, and the conditions are similar to ones that are used to clean silicon substrates (these will depend on the type of plasma generator): Exemplary conditions are

Oxygen plasma treatment at room temperature
Applied radio frequency (RF): 13.56 MHz
RF power: 10 - 100 W
O_2 pressure: 0.1 - 1 mbar
Time: 10 seconds to 5 minutes

In one embodiment, after polymerization an amine-reactive compound, such as carboxylic acid anhydride, is added and reacted with the modified carbon nanotubes.

It is preferred that the modified carbon nanotubes are dissolved in aqueous solution.

The object of the present invention are also solved by a method of solubilizing carbon nanotubes, comprising the steps:

a) providing, in any order:

    carbon nanotubes, and

urea;

b) mixing together the nanotubes and the urea;

c) heating the mixture of b).

Preferably, the carbon nanotubes are as defined above.

Preferably, the heating is above the melting temperature of urea, wherein, more preferably, the heating is in the range of approximately 130°C – 180°C, even more preferably approximately 150°C – 170°C, most preferably approximately 160°C.

In one embodiment, the heating is for approximately 1 - 60 min, preferably approximately 3 - 20 min, more preferably approximately 5 - 15 min.

In one embodiment, the product of step c) is dissolved in aqueous solution and subjected to a size-separation step and/or an adsorption step and/or an enzymatic degradation step and/or a washing and filtration step and/or a precipitation step and/or a selective burning step and/or a plasma treatment step.

The objects of the present invention are also solved by a carbon nanotube, produced by the method according to the present invention.

Preferably the nanotube is non-bundled.

In one embodiment, the carbon nanotube is decorated in a pearl chain-like manner with discrete bodies, when viewed under AFM.

In one embodiment these discrete bodies are polymeric, "polymeric", in this context meaning "comprising polymers".

Preferably, the carbon nanotube has one or more physical characteristics selected from the group comprising:

- an absorption maximum between 215 nm and 245 nm,
- an emission maximum between 500 nm and 550 nm, when excited with UV or blue light (330 nm – 430 nm), and

- absorption maxima in the infrared in the following wavenumber regions:
  $3350 - 3360\ cm^{-1}$, $1665 - 1675\ cm^{-1}$, $1595 - 1605\ cm^{-1}$, and $1425 - 1435\ cm^{-1}$.

It has to be said, though, that the inventors do not wish to be limited to the notion that these physical properties are intrinsic to the nanotubes themselves. These characteristics may also be due to the discrete bodies attached to the nanotubes.

The objects of the present invention are also solved by an association of carbon nanotubes according to the present invention, wherein the carbon nanotubes are non-bundled, but interconnected at their ends through said discrete bodies into branched structures, when viewed under AFM.

The objects of the present invention are also solved by the use of a carbon nanotube or of an association of carbon nanotubes according to the present invention in an electronic device, a filled polymer composite, a field emission device, an energy conversion device, a nanoprobes, gas sensor, an electromechanical device and/or a nanoelectronic device.

It should be understood that the mixing of the carbon nanotubes and the at least one type of monomer (or the precursor thereof, or urea etc.) can be achieved by various means, such as are well known to someone skilled in the art. These include, but are not limited to grinding, milling, in particular ball-milling, sand-milling etc. Furthermore it is clear that the carbon nanotubes provided can be treated with other methods that are commonly known to someone skilled in the art. For example they may, before or after the reaction of the present invention, be ultra-sonicated, they may be heated in a vacuum or under inert atmosphere or they may be further functionalized. If they are thermally annealed (heated) and this takes place after the reaction of the invention, this may remove the functionalization achieved by the reaction of the invention and even reverse the effects of a previous oxidative treatment. Such a subsequent thermal annealing treatment may be necessary to restore the electronic properties of pristine carbon nanotubes. Temperatures in the range of approximately 200 – 1200°C are effective for this purposes. It is also clear that various means of size separation can be used, so as to separate unreacted small molecule parts from the reacted portions. For example appropriate gel-filtration material, chosen by the experimenter depending on the desired size exclusion, can be used. Various grades of Sephadex gel-filtration material seem to be appropriate in a preferred embodiment, for example Sephadex G-100 or G-10. However other types of

Sephadex and dextran-based materials can be used instead, the only criterion being that an effective separation of small molecules from portions/compounds having undergone the reaction(s) of the present invention takes place. Furthermore, small molecules and non CNT-particles and/or non-modified CNTs may be removed by adsorption to a gelfiltration material, which material may be the same as defined above for the size-exclusion step. Furthermore, small molecules can also be removed by the use of appropriate degradation enzymes, e. g. urease in the case of urea. Another way of separation is selective precipitation of (modified) CNTs, e. g. by means of perchlorate, in particular sodium perchlorate.

As used herein, the term "precursor" is meant to encompass any chemical entity that is capable of providing monomers for a subsequent polymerization reaction. The term "monomer", as used herein, is meant to encompass any chemical entity that is capable of reacting with like molecules and thereby form a larger entity comprising more than one of the original monomers. It is clear that the term "monomer" also encompasses "oligomers" which are still capable of undergoing a polymerization reaction.

A reaction or polymerization is said to occur "at the functional groups" in the sense that the growing polymer chain or reaction product, at one of its ends, is either covalently bonded to a functional group/functional groups or non-covalently adsorbed thereto, or both, in the sense that within one experimental set-up some growing polymer chains or reaction products are covalently bonded to functional group and other polymer chains or reaction products are non-covalently adsorbed thereto. The term "occurs at the functional groups", as used herein, is used interchangeably with "is initiated by the functional groups". It can also mean that the functional groups serve as initiation sites for polymerization. In doing so, the functional groups may either serve directly as a site where polymerization occurs or they may first be converted to a functional group at which then the polymerization occurs. Preferably this conversion is due to the monomer molecules and/or their precursor and/or a decomposition product of the monomer or its precursor. An example for the latter reaction can be seen from figure 3 in "Reactions involving epoxide groups", where ammonia, a decomposition product of urea, converts an epoxide to an amine and an OH-group where then polymerization takes place.

It should also be understood that the heating step according to the present invention can be performed by any conventional heating means, e. g. an oven, hot plate, oil bath or heat gun. In

one embodiment it is performed using a heat gun.

"Derivatives of urea" are e. g. nitrourea, urea hydrochloride, urea hydrogen peroxide, urea nitrate, and ammonium carbamate, all of which can act as sources of ultimately isocyanic acid.

It has surprisingly been found that performing a polymerization reaction on the carbon nanotubes, in effect, exfoliates the tubes and solubilizes them such that afterwards they are present as single, non-bundled entities. The method according to the present invention, as opposed to prior-art-methods, yields non-bundled carbon nanotubes, i. e. tubes which are not in an association of essentially parallel CNTs that are in contact with each other. A preferred polymerization reaction that is taking place on the carbon nanotubes is the polymerization of isocyanic acid/cyanate as a decomposition product of urea, to from polyisocyanate appendages. Urea has often been used as a source of isocyanic acid. For such purposes, urea can either be used neat in the molten state (mp 133 °C), or dissolved in water or an organic solvent. Alternative exemplary sources of isocyanic acid include a) thermal depolymerization of cyanuric acid or isocyanuric acid, b) hydrolysis of cyanuric chloride and subsequent depolymerization of the resultant cyanuric acid, c) acidification of cyanate salts, d) hydrolysis of trichloroisocyanic acid and subsequent depolymerization of the resultant isocyanuric acid, and e) thermal decomposition of nitrourea (Davis et al., 1929, J. Am. Chem. Soc. 51, 1790). All these sources of isocyanic acid are to be understood as "precursors of the at least one type of monomer" where isocyanic acid or cyanate ion is the monomer in the present invention.

In the following, the chemistry of urea and isocyanic acid/cyanate is further explained.

Despite its simple structure, the chemistry of urea (NH_2CONH_2) can be quite complex, mainly because of the extremely reactive nature of one of its decomposition products, isocyanic add (HNCO). It is often assumed that an equilibrium exists between urea and ammonium cyanate (NH_4CNO):

$$NH_2CONH_2 \Leftrightarrow NH_4CNO, \quad (1)$$

The synthesis of urea from ammonium cyanate by Wöhler was the first example of an "organic" compound being synthesized in the laboratory from purely "inorganic" ones. Much

of the current interest in the chemistry of urea stems from its possible role in pre-biotic evolution, as well as its importance as a fertilizer.

Since ammonium ion (NH_4^+) is weakly acidic and cyanate ion (CNO^-) is weakly basic, the equilibrium in equation (1) can be extended to include ammonia (NH_3) and cyanic add (CNOH):

$$NH_4CNO \Leftrightarrow NH_3 + CNOH \quad (2)$$

While cyanic acid is stable enough to be isolated, isocyanic add is the thermodynamically favored isomer under normal conditions.

$$CNOH \Leftrightarrow HNCO \quad (3)$$

Both isomers are very chemically reactive.

Isocyanates (RNCO), which are organic derivatives of isocyanic acid, are also very reactive and undergo a great many reactions, especially addition reactions with compounds containing active hydrogen and polymerization (self-addition). Several of these reactions are listed below and are representative of the reactions of isocyanic acid (where R = H) as well.

1. Reaction with alcohols and phenols to form urethanes:
   $$RNCO + HOR' \rightarrow RNH\text{-}CO\text{-}OR' \quad (4)$$

2. Reaction with amines to form ureas:
   $$RNCO + H_2NR' \rightarrow RNH\text{-}CO\text{-}NHR' \quad (5)$$

3. Reaction with carboxylic acids to form amides:
   $$RNCO + HOOCR' \rightarrow RNH\text{-}COR' + CO_2 \quad (6)$$

4. Reaction with urethanes to form allophanates:
   $$RNCO + R'NH\text{-}CO\text{-}OR'' \rightarrow RNH\text{-}CO\text{-}NR'\text{-}CO\text{-}OR'' \quad (7)$$

5. Reaction with ureas to form biurets:

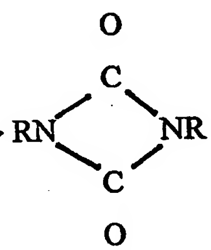
$$RNCO + R'NH\text{-}CO\text{-}NHR'' \rightarrow RNH\text{-}CO\text{-}NR'\text{-}CO\text{-}NHR'' \quad (8)$$

6. Reaction with amides to form acylureas:

$$RNCO + R'NH\text{-}COR'' \rightarrow RNH\text{-}CO\text{-}NR'\text{-}COR'' \quad (9)$$

7. Dimerization to form uretidiones:

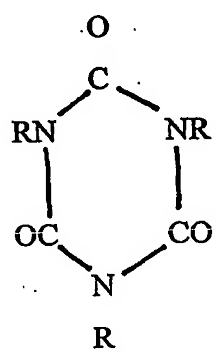
2 RNCO →



(10)

8. Trimerization to form isocyanurates:

3 RNCO →



(11)

9. Hydrolysis to form amines:

$$RNCO + H_2O \rightarrow RNH_2 + CO_2 \quad (12)$$

Urea has often been used as a source of isocyanic acid for the above reactions. For such purposes, urea can either be used neat in the molten state (mp 133 °C), or dissolved in water or an organic solvent. Alternative sources of isocyanic acid include thermal depolymerization of cyanuric acid, isocyanuric acid, hydrolysis of cyanuric chloride and subsequent depolymerization of the resultant cyanuric acid acidification of cyanate salts, hydrolysis of trichloroisocyanic acid and subsequent depolymerization of the resultant isocyanuric acid, and thermal decomposition of nitrourea (Davis et al., 1929, J. Am. Chem. Soc. 51, 1790). All these sources of isocyanic acid are to be understood as "precursors of the at least one type of monomer" where isocyanic acid or cyanate ion is the monomer in the present invention.

Formaldehyde (or paraformaldehyde) reacts with urea to form addition products with hydroxymethyl end groups or methylene bridges between urea units:

$$H_2NCONH_2 + CH_2O \rightarrow H_2NCONHCH_2OH \quad (13)$$

$$H_2NCONHCH_2OH + H_2NCONH_2 \rightarrow H_2NCONHCH_2NHCONH_2 + H_2O \quad (14)$$

Such urea-formaldehyde condensation products are industrially important in materials ranging from plastics and adhesives to fertilizers.

Furthermore, urea is able to form solid-state inclusion compounds (or „clathrates") with long-chained hydrocarbons such as *n*-alkanes. The host structure consists of continuous one-dimensional channels *(ca* 0.6 nm diameter) constructed from an essentially infinite three-dimensional hydrogen-bonded network of urea molecules. (Steed, J. W.; Atwood, J. L (2000) *Supramolecular Chemistry;* John Wiley & Sons, Ltd., Chichester, pp. 272-277) The urea channel structure is only stable when occupied. Urea inclusion compounds based on a layered structure (Lee et al. (2001) *J. Am. Chem. Soc.* **123**, 12684) as well as inclusion compounds involving both urea and one of its decomposition products (Mak et al. (1995) *J. Am. Chem. Soc.* **117**, 11995) are also known.

In the following reference is made to the figures, wherein

Figure 1: shows UV-visible absorption spectra of RFP-SWNTs treated with molten urea and then dissolved in water, before (dashed curve) and after (continous curve) removal of components with high affinity for cross-linked dextran (Sephadex® G-100).

Figure 2: shows a tapping mode AFM image from a solution of urea-treated RFP-SWNTs applied to a film of polystyrene on mica. The solution used was the one whose UV-visible spectrum is shown in Figure 1 (continuous curve) and was applied to the film by a spin-coating process.

Figure 3: shows the postulated chemical reactions involved in the modification of CNTs by treatment with molten urea. The CNTs were previously treated to generate oxidized carbon

groups, mainly at nanotube ends and sidewall defects. The three oxidized carbon groups implicated are carboxylic acid, phenol, and epoxide, but other groups could also be involved.

Figure 4: shows UV-visible absorption spectra of RFP-SWNTs treated with molten urea and then dissolved in water according to Example 1 (see below), after fractionation by column chromatography over Sephadex® G-100 into Solution B1 and Solution B2 according to Example 4. Solution B1 was diluted by a factor of 2.5 to obtain the spectrum shown.

Figure 5: shows emission spectra of Solution B1 (diluted by a factor of 2.5) and Solution B2 from Example 4 (see below) when excited with 410-nm light. The absorption spectra of these samples are shown in Figure 4.

Figure 6: shows UV-visible absorption spectra of RFP-SWNTs treated with molten urea and then dissolved in water according to Example 5 (see below), before and after fractionation by column chromatography over Sephadex® G-10 according to Example 6 (see below). Solution C (before fractionation) was diluted by a factor of 100 to obtain the spectrum shown (dashed curve). Solution D1 (first fraction) was diluted by a factor of 25 to obtain the spectrum shown (continuous curve). Solution E was obtained from the second fraction by precipitation with sodium perchlorate and re-dissolution in water (dash-dotted curve).

Figure 7: shows emission spectra of Solution D1 (diluted by a factor of 25) and Solution E from Example 6 and Example 7 (see below), respectively, when excited with 410-nm light. The absorption spectra of these samples are shown in Figure 6. The signal from a solution of water alone is also shown (dotted curve).

Figure 8: shows the infrared absorption spectrum of a solid film obtained by drying Solution D1 from Example 6 (see below) onto a calcium fluoride disk.

The invention will now be further described and better understood by the following examples which are presented for illustrative, non-limiting purposes.

Example 1

Modification of CNTs using urea melt

The CNTs used for these experiments were purchased from Carbon Solutions, Inc. (5094 Victoria Hill Drive, Riverside, CA 92506). The product name is RFP-SWNT. According to information provided by the supplier, RFP-SWNT is prepared from their product named AP-SWNT by acid purification with subsequent processing to reduce functionality. The AP-SWNT product consists of single-walled CNTs prepared by the electric arc method. Hu *et al.* (2001)[47] determined the mole percentage of acid sites (including carboxylic acids, lactones, and phenols) relative to the total amount of carbon in RFP-SWNTs by acid-base titration and found 1%, of which 0.7-0.8% could be attributed to carboxylic acid groups. The percentages found for the CNTs without the processing step to reduce functionality were 2.7% (total acid sites) and 2.1-2.2% (carboxylic acid groups). Thus it can be concluded that the process used to reduce the functionality of acid purified AP-SWNT CNTs reduces it by approximately two-thirds. The degree of functionality on RFP-SWNT is still appreciable, however, approximately one carbon per 100 being bonded to at least one oxygen atom to produce an acidic site, approximately three-quarters of which are -COOH groups. These groups are expected to be located predominantly at nanotube ends and sidewall defect sites.

RFP-SWNT (2.46 mg) was placed in a glass test tube (Schott Duran®, 12 x 100 mm) and pulverized with a glass stirring-rod (5 mm diameter). Urea (98.5 mg) was added and thoroughly pulverized with the RFP-SWNT to yield a gray powder. The powder was heated by placing the bottom of the test tube at the exit port of a heat gun (Steinel Typ 3449, 2000 W) set to have a maximum temperature at the exit of 160 °C. The powder melted to give a black liquid, which was kept agitated by rotating and shaking the tube manually. After 10 minutes, the mixture was allowed to cool to room temperature, yielding a black solid. Water (0.50 ml) was added to the solid, which appeared to dissolve completely within a few seconds by simple mixing, giving a dark black solution. A small volume (10 μl) of the solution was diluted with water (1000 μl) in a quartz cuvette and the UV-visible absorption spectrum was recorded. The spectrum is shown in Figure 1 (dashed curve). The solution in the test tube was transferred to a small polypropylene centrifuge tube together with the solution in the cuvette. It was centrifuged at 5000 rpm for 10 minutes two times. The pH of the solution was 8.15.

Example 2

Chromatography over Sephadex G-100

Two drops (approximately 50 μl) of the centrifuged solution from Example 1 were applied to

a small column (7 x 45 mm) of Sephadex® G-100 swollen in water. After entering the column bed, the solution was eluted with water. A gray band moved through the column and was collected. Another gray band remained at the top (1-2 mm) of the column bed and could not be washed out. The solution that was collected was transferred to a quartz cuvette, diluted with water (total volume approximately 0.7 ml), and the UV-visible absorption spectrum was recorded. The spectrum is shown in Figure 1 (continuous curve). It shows a nearly featureless rise in absorption from 1000 nm to 300 nm and a maximum at 242 nm. This solution is referred to below as Solution A.

Example 3

AFM measurements

AFM measurements were made using a Digital Instruments Dimension 3100 SPM System with NanoScope IV Controller and Olympus OMCL AC160TS Micro Cantilever.

A substrate for AFM measurements was prepared by applying a drop of a 2.5 wt-% solution of polystyrene (Aldrich #44.114-7. average M_w *ca.* 350.000) in toluene to a mica substrate. The substrate was rotated at 600 rpm while a drop (20 µl) of Solution A (undiluted) was applied to the center. The rotation rate was increased to 700 rpm, causing most of the solution to be ejected from the substrate. Afterwards, spinning it at 4000 rpm for 90 s dried the substrate. An AFM image obtained by scanning at a location near the center of the substrate is shown in Figure 2, together with a zoomed-in section of the image.

The fact that the RFP-SWNT material becomes water-soluble after melting its powdered mixture with urea is most likely due to covalent modification of the CNTs or non-covalent adsorption of water-soluble polymer products. While not intending to be limited to any particular theory, the present inventors favor the covalent modification possibility due to the fact that the same process fails to render as-prepared single-walled CNTs water-soluble. As noted above, roughly one carbon atom per 100 of the CNTs in RFP-SWNT is in a chemically oxidized acidic state, based on the results of Bower et al. ((1998) *Chem. Phys. Lett.* **288**, 481). Of the functional groups responsible for such sites, -COOH and phenolic -OH groups are reactive with isocyanates, including isocyanic acid. The reaction of isocyanic acid with these groups and subsequent addition reactions to generate polyisocyanate appendages are shown schematically in Figure 3. High molecular weight polyisocyanates were first reported in 1959 and

represent the simplest type of nylon (nylon-1) (Bur et al. (1976) *Chem. Rev.* 76, 727). Another possible reaction shown in Figure 3 is the ring opening of epoxide groups by ammonia to generate amine and alcohol groups, which then react with isocyanic acid. Lu *et al.* (2002) (*J. Phys. Chem.* B 106, 2136) recently proposed using the ring-opening step as a way to functionalize the sidewalls of single-walled CNTs. It should be noted that polymer chain branching and cross-linking reactions are also possible, since the H-atoms bonded to the N-atoms of the linear chains are expected to be reactive with isocyanic acid.

The growth of polyisocyanate on the RFP-SWNTs could account for the water-solubility of the product as well as the dissociation of nanotube bundles into individual tubes, as is indicated by the AFM images. The discrete round-shaped bodies seen attached in a pearl chain-like manner to the CNTs in the AFM images are presumably the polymers. The sizes of the bodies of several nanometers suggest polymer molecular weights of the order of 10,000.

Since the CNTs in the RFP-SWNT material are expected to occur in bundles, the growth of polyisocyanate uniformly along the nanotubes, as the AFM results suggest, indicates that dissociation of the bundles occurred at an early stage of the reaction. This surprising result implicates the tendency of urea to form inclusion compounds. Although the channel in the usual inclusion compounds between urea and hydrocarbons are much too small to accommodate CNTs, the transient formation of larger cages should be considered. Urea is also widely used for denaturing proteins, which involves the disruption of non-covalent bonds within proteins, including van der Waals interactions. Since van der Waals interactions are important for the bundling of CNTs, the ability of urea to cause dissociation may be related to its ability to denature proteins.

Example 4

Chromatography over Sephadex® G-100

A 250-µL aliquot of the centrifuged solution from Example 1 was applied to a small column (10 x 80 mm) of Sephadex® G-100 swollen in water. After entering the column bed, the solution was eluted with water. Once the eluting solution became colored (black-brown), 1.1 mL was collected: this solution is referred to below as Solution B1. The next 1.5 mL (yellow colored) was also collected and is referred to as Solution B2. A black-brown band remained at the top (~5 mm) of the column and could not be washed out with water. The UV-visible

absorption spectra of these two solutions are shown in Figure 4. The spectrum of Solution B1 (after dilution with water by a factor of 2.5) is characterized by a maximum at 235 nm and a tailing absorption to beyond 1000 nm (Figure 4, continuous curve), weak but distinct inflections occur in the wavelength region 400-500 nm. The spectrum of Solution B2 (Figure 4, dashed curve) is characterized by a slightly structured absorption in the wavelength region 400-500 nm and almost no absorption beyond 700 nm. There is no obvious maximum in the UV region. Despite this difference in absorption spectral characteristics, both solutions have a yellow emission with a maximum near 515 nm (Figure 5). The emission from Solution B2 is 4 times more intense than that from B1, despite that fact that the absorbance of B1 is 4.5 times greater than the absorbance of B2 at the excitation wavelength (410 nm). Thus it can be concluded that two (or more) components contribute to the absorption and emission properties of Solution B1. One contribution is due to the characteristics of functionalized CNTs (plasmon absorption maximum below 250 nm, structure-less absorption tail into the near infrared, and little or no emission). The other contribution is due to a component that is also present in Solution B2 with a yellow emission maximum 515 nm. This component is likely to be responsible for absorption between 400 nm and 500 nm in both solutions. It is a product of the reaction between the RFP-SWNT and molten urea and appears to be the component that makes the CNTs soluble in water.

Example 5

Modification of CNTs using urea melt

RFP-SWNT (12.6 mg) was pulverized with urea (504 mg) in a glass test tube as described in Example 1. The powdered mixture was heated with a heat gun source as in Example 1 for 7.5 minutes, cooled, mixed with water (800 μL) water, and centrifuged (5000 rpm for 10 min). The resulting solution, referred to below as Solution C, had a pH of 9.6. A small volume (10 μl) of the solution was diluted with water (1000 μl) in a quartz cuvette and the UV-visible absorption spectrum was recorded. The spectrum, shown in Figure 6 (dashed curve), has a tailing absorption to beyond 1000 nm. No maximum is apparent in the UV region due to absorption by urea and by-products of the reaction.

Example 6

Chromatography over Sephadex® G-10

A 500-μL aliquot of the centrifuged solution from Example 5 was applied to a small column (10 x 52 mm) of Sephadex® G-10 swollen in water. After entering the column bed, the solu-

tion was eluted with water. Once the eluting solution became colored (black-brown), 1.0 mL was collected: this solution is referred to below as Solution D1. The next 0.9 mL (black-brown colored) was also collected and is referred to as Solution D2. A light gray band remained at the top (~11 mm) of the column and could not be washed out with water. The UV-visible absorption spectrum of Solution D1 (after dilution with water by a factor of 25) is characterized by a maximum at 220 nm and a tailing absorption to beyond 1000 nm (Figure 6, continuous curve). The diluted Solution D1 is characterized by a yellow emission with a maximum near 515 nm (Figure 7, continuous curve).

Example 7

Isolation of modified CNTs by precipitation with sodium perchlorate

Sodium perchlorate monohydrate (115 mg) was added to Solution D2 from Example 6, and then mixed until the crystals dissolved, giving a concentration of $NaClO_4$ of ~1.0 M. The solution became opalescent within minutes. After being left overnight, a black precipitate settled out leaving clear yellow-brown supernatant, which emitted yellow-white light when excited with UV (366 nm) light. After removing the supernatant, the precipitate was readily re-dissolved in 500 µL of water (Solution E). The UV-visible absorption spectrum of Solution E (after dilution with water by a factor of 20) is characterized by a maximum at 242 nm and a tailing absorption to beyond 1000 nm (Figure 6, dash-dotted curve). The diluted solution is also characterized by a weak yellow emission whose maximum is near 550 nm (Figure 7, dash-dotted curve). Sodium perchlorate monohydrate (115 mg) was added to Solution E, and then mixed until the crystals dissolved, giving a concentration of $NaClO_4$ of ~0.25 M. The solution became opalescent within minutes. After 30 minutes, it was centrifuged at 5000 rpm for 10 minutes, yielding a black precipitate and clear colorless supernatant. After removing the supernatant, the precipitate was dried under a gentle stream of compressed air. The resulting solid, having a mass of 0.47 mg, re-dissolved in 10 µL of water after bath sonication for 1 minute.

Example 8

FTIR measurements

Solution D1 from Example 6 was evaporated to dryness under a gentle stream of compressed air, yielding 0.46 mg of glassy solid. A 10-µL aliquot of water was added to the solid, which dissolved readily. A 10-µL aliquot of methanol was added to the solution, causing precipitation. This suspension was applied to a polished calcium fluoride disk (20 mm diameter x 2

mm thick) and allowed to dry under ambient conditions, producing a black film. The FTIR measurement was performed in normal transmission mode with a Bruker IFS 66 /S spectrometer. The spectrum, shown in Figure 8, has several absorption bands that are characteristic of urea derivatives: 3435, 3352, 1670, 1603, 1432, and 1165 cm^{-1} (Lee *et al.* (1987) *Macromolecules* **20**, 2089; Pollack *et al.* (1989) *Macromolecules* **22**, 551; Eaton *et al.* (1996) *Macromolecules* **29**, 2531; Marcos-Fernández *et al.* (1997) *Macromolecules* **30**, 3584; Keuleers *et al.* (1999) *J. Phys. Chem. A* **103**, 4621).

The scenario that is envisaged by the present inventors is the intercalation of the CNT bundles by urea, urea decomposition, addition reactions between the decomposition products and oxidized carbon groups on the CNTs, and polymer growth from those sites. These processes may begin with the grinding together of the CNTs and urea, which may also result in mechanical cutting of the CNTs.

The procedure described in this report of invention has several of the characteristics that were listed above for the ideal procedure:

1. It is relatively simple and fast.
2. It yields isolated CNTs that dissolve in water.
3. It is applicable for CNTs that have not been shortened.
4. It provides soluble CNTs with functional groups for subsequent chemical modification.

Further, the procedure is applicable for multi-walled CNTs. It is also clear that suitable chemical modifications, introduced either during the reaction or afterwards, are possible for making the CNTs soluble in a variety of organic solvents. It may be impossible to perform such reactions without altering the electronic and/or mechanical properties of the CNTs, but it may be possible to restore them finally by thermal treatment under vacuum or inert atmosphere. None of the state of the art procedures offer this combination of features.

The features disclosed in the foregoing description and the claims may, both separately and in any combination thereof be material for realizing the invention in diverse forms thereof.

List of references cited in Table 1

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FB12112

EPO - Munich
46
12. Dez. 2002

Claims

1. A method of solubilizing carbon nanotubes, comprising the steps:
   a) providing, in any order:
      carbon nanotubes, and
      at least one type of monomer molecules capable of undergoing a polymerization reaction or a precursor of the at least one type of monomer molecules;
   b) mixing together the nanotubes with the monomer molecules or their precursor;
   c) initiating a polymerization reaction of the monomer molecules

   to yield modified carbon nanotubes.

2. The method according to claim 1, wherein the carbon nanotubes have functional groups on their surface and/or ends.

3. The method according to claim 2, wherein the functional groups are oxygenated functional groups selected from the group comprising C-O species (alcohol, phenol, ether, epoxide), C=O species (aldehyde, ketone, quinone), and O-C=O species (carboxylic acid, ester, anhydride, lactone).

4. The method according to any of the foregoing claims, wherein the carbon nanotubes are single-walled or multi-walled nanotubes.

5. The method according to any of the foregoing claims, wherein approximately 1 per approximately 200 to 1 per 10 carbon atoms of the carbon nanotubes are in an oxidized state.

6. The method according to any of the foregoing claims, wherein approximately 1 per approximately 150 to 1 per 20 carbon atoms of the carbon nanotubes are in an oxidized state.

7. The method according to claim 6, wherein approximately 1 per 100 carbon atoms of the carbon nanotubes are in an oxidized state.

8. The method according to any of claims 2 – 7, wherein the polymerization occurs at the functional groups.

9. The method according to any of the foregoing claims, wherein the monomer molecules are isocyanic acid and/or cyanate ion.

10. The method according to claim 9, wherein the precursor of the at least one type of monomer molecules is urea and/or its derivatives.

11. The method according to claim 9, wherein the precursor of the at least one type of monomer molecules is selected from the group comprising cyanuric acid, cyanuric chloride, isocyanuric acid and trichloroisocyanic acid.

12. The method according to claim 9, wherein the precursor is a cyanate salt.

13. The method according to any of the foregoing claims, comprising the additional step(s):
ba) heating the mixture, or, alternatively,
bb) acidifying the mixture or,
both steps ba) and bb).

14. The method according to claim 13, wherein the heating and/or acidifying is such, that the precursor of the at least one type of monomer molecules is induced to form said monomer molecules.

15. The method according to any of the foregoing claims, wherein the at least one type of monomer molecules or the precursor of the at least one type of monomer molecules is provided in a solvent.

16. The method according to any of the foregoing claims, wherein the carbon nanotubes are provided in a solvent.

17. The method according to claims 15 – 16, wherein the solvent of claim 15 is the same as the solvent of claim 16, or wherein the solvents are different.

18. The method according to any of claims 15 – 17, wherein the solvent(s) can be heated to a temperature close to or above the melting point of the monomer or its precursor, without decomposing or evaporating.

19. The method according to any of the foregoing claims, wherein, before or after the polymerization reaction, aldehydes are added to the mixture.

20. The method according to claim 19, wherein the aldehydes are selected from the group comprising formaldehyde, acetaldehyde, paraformaldehyde, propionaldehyde, benzaldehyde, and glutaraldehyde.

21. The method according to any of the foregoing claims, wherein, after step c), non-reacted monomer and/or precursor is removed from the reaction.

22. The method according to claim 21, wherein the removal occurs by a size separation step and/or an adsorption step and/or by enzymatic degradation, and/or filtration and washing, and/or precipitation, and/or selective burning and/or plasma treatment.

23. The method according to claim 22, wherein the size separation and/or adsorption occurs by gelfiltration, and the enzymatic degradation occurs by means of urease, and the precipitation occurs by perchlorate.

24. The method according to any of the foregoing claims, wherein after polymerization an amine-reactive compound, such as carboxylic acid anhydride, is added and reacted with the modified carbon nanotubes.

25. The method according to any of the foregoing claims, wherein the modified carbon nanotubes are dissolved in aqueous solution.

26. A method of solubilizing carbon nanotubes, comprising the steps:
   a) Providing, in any order:
      carbon nanotubes, and
      urea;
   b) mixing together the nanotubes and the urea;

c) heating the mixture of b).

27. The method according to claim 26, wherein the carbon nanotubes are as defined in any of claims 2 – 7.

28. The method according to any of claims 26 – 27, wherein the heating is above the melting temperature of urea.

29. The method according to claim 28, wherein the heating is in the range of approximately 130°C – 180°C, preferably approximately 150°C – 170°C, more preferably approximately 160°C.

30. The method according to any of claims 26 – 29, wherein the heating is for approximately 1 – 60 min, preferably approximately 3 – 20 min, more preferably approximately 5 – 15 min.

31. The method according to any of claims 26 – 30, wherein the product of step c) is dissolved in aqueous solution and subjected to a size-separation step and/or an adsorption step and/or an enzymatic degradation step and/or a washing and filtration step and/or a precipitation step and/or a selective burning step and/or a plasma treatment step.

32. A carbon nanotube, produced by the method according to any of claims 1 – 31.

33. The carbon nanotube according to claim 32, wherein the nanotube is non-bundled.

34. The carbon nanotube according to any of claims 32 – 33, wherein it is decorated in a pearl chain-like manner with discrete bodies, when viewed under AFM.

35. The carbon nanotube according to any of claims 32 – 34, having one or more physical characteristics selected from the group comprising:
- an absorption maximum between 215 nm and 245 nm,
- an emission maximum between 500 nm and 550 nm, when excited with UV or blue light (330 nm – 430 nm), and
- absorption maxima in the infrared in the following wavenumber regions:

$3350 - 3360\ cm^{-1}$, $1665 - 1675\ cm^{-1}$, $1595 - 1605\ cm^{-1}$, and $1425 - 1435\ cm^{-1}$.

36. An association of carbon nanotubes according to any of claims 34 – 35, wherein the carbon nanotubes are non-bundled, but interconnected at their ends through said discrete bodies into branched structures, when viewed under AFM.

37. Use of a carbon nanotube according to any of claims 32 – 35 or of an association of carbon nanotubes according to claim 36 in an electronic device, a filled polymer composite, a field emission device, an energy conversion device, a nanoprobe, a gas sensor, an electromechanical device and/or a nanoelectronic device.

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Abstract

The present invention relates to a method of solubilizing carbon nanotubes, to carbon nanotubes produced thereby and to uses of said carbon nanotubes.

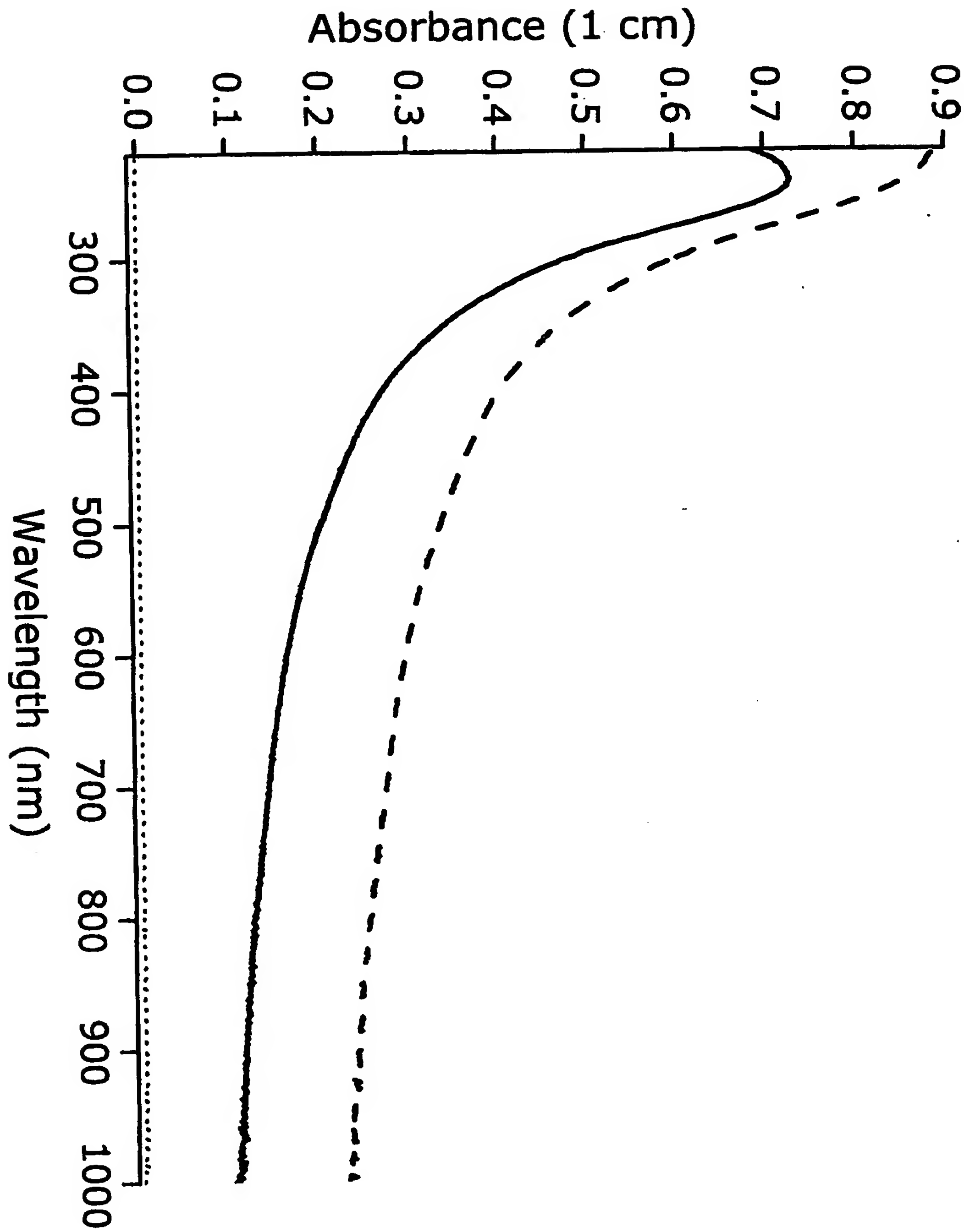

Absorbance (1 cm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
300
400
500
600
700
800
900
1000
Wavelength (nm)

Figure 1

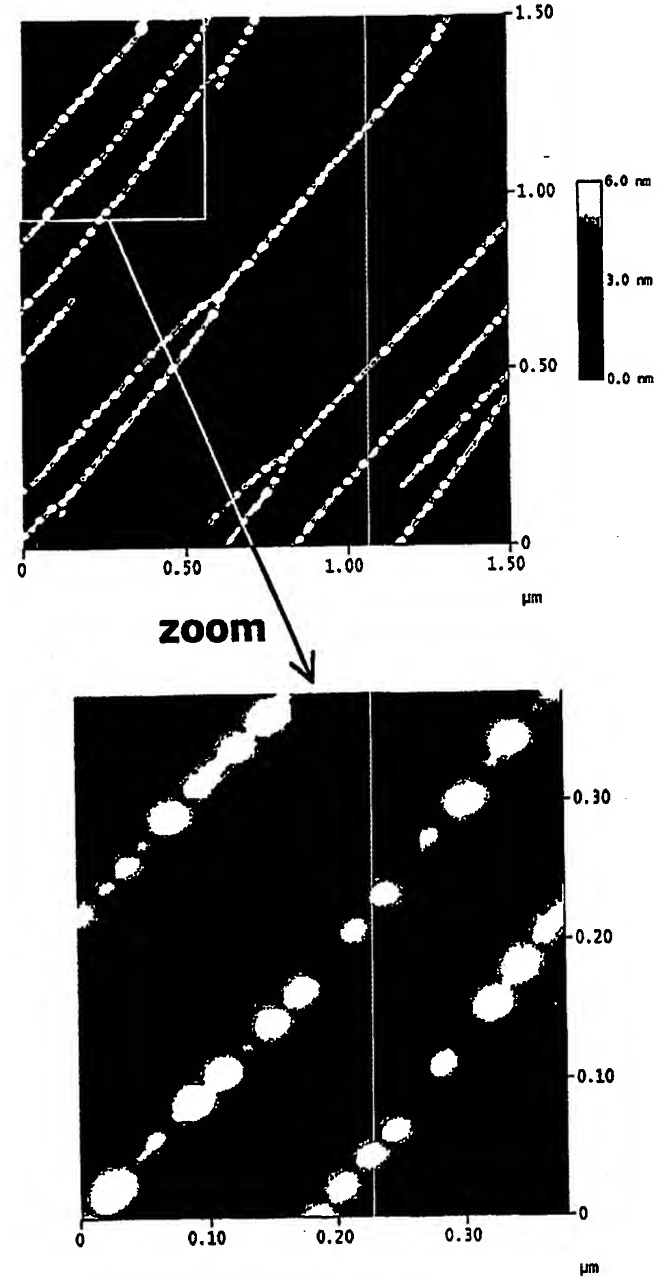


Figure 2

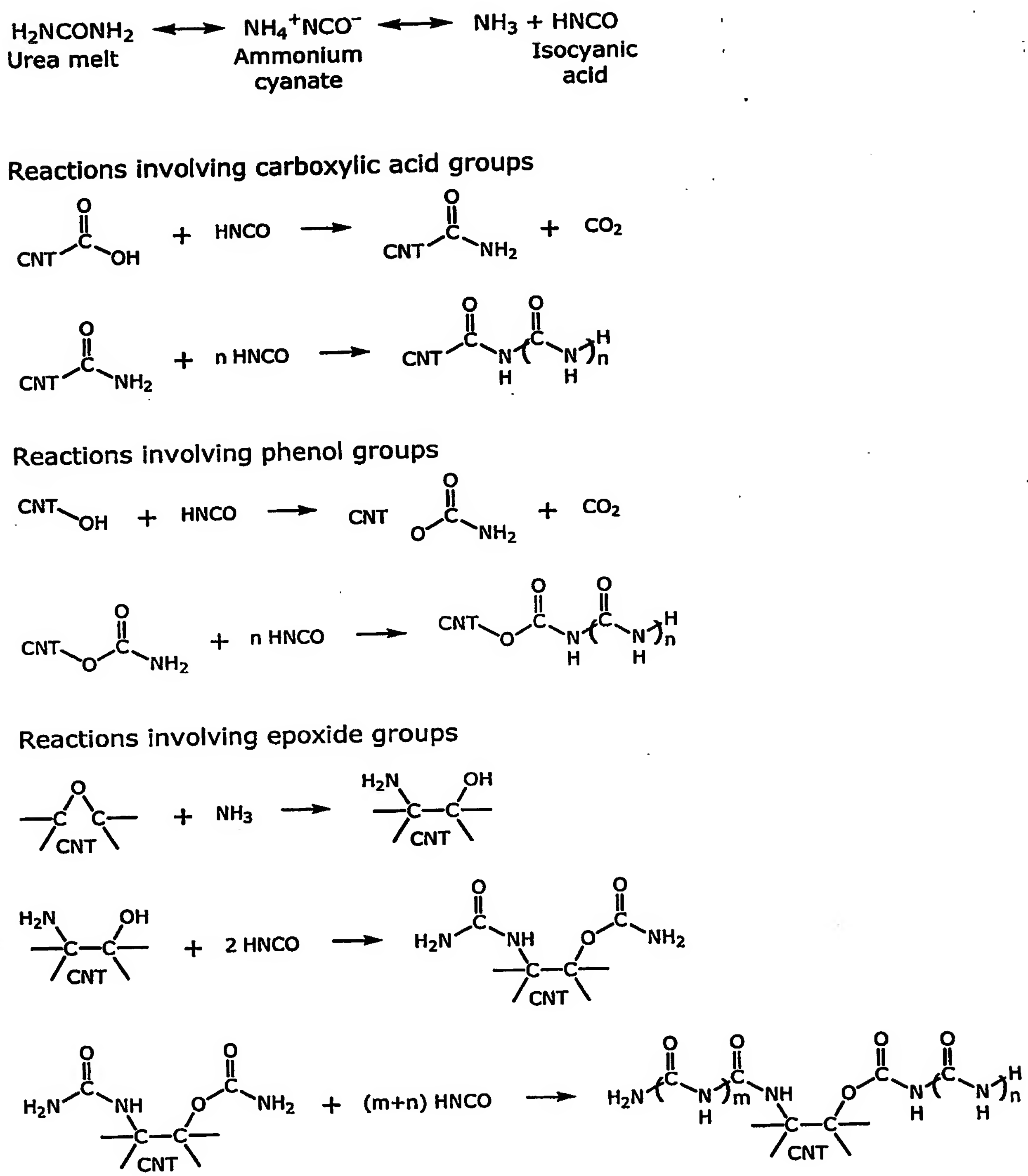

H2NCONH2
Urea melt
NH4+NCO-
Ammonium cyanate
NH3 + HNCO
Isocyanic acid
Reactions involving carboxylic acid groups
Reactions involving phenol groups
Reactions involving epoxide groups

Figure 3

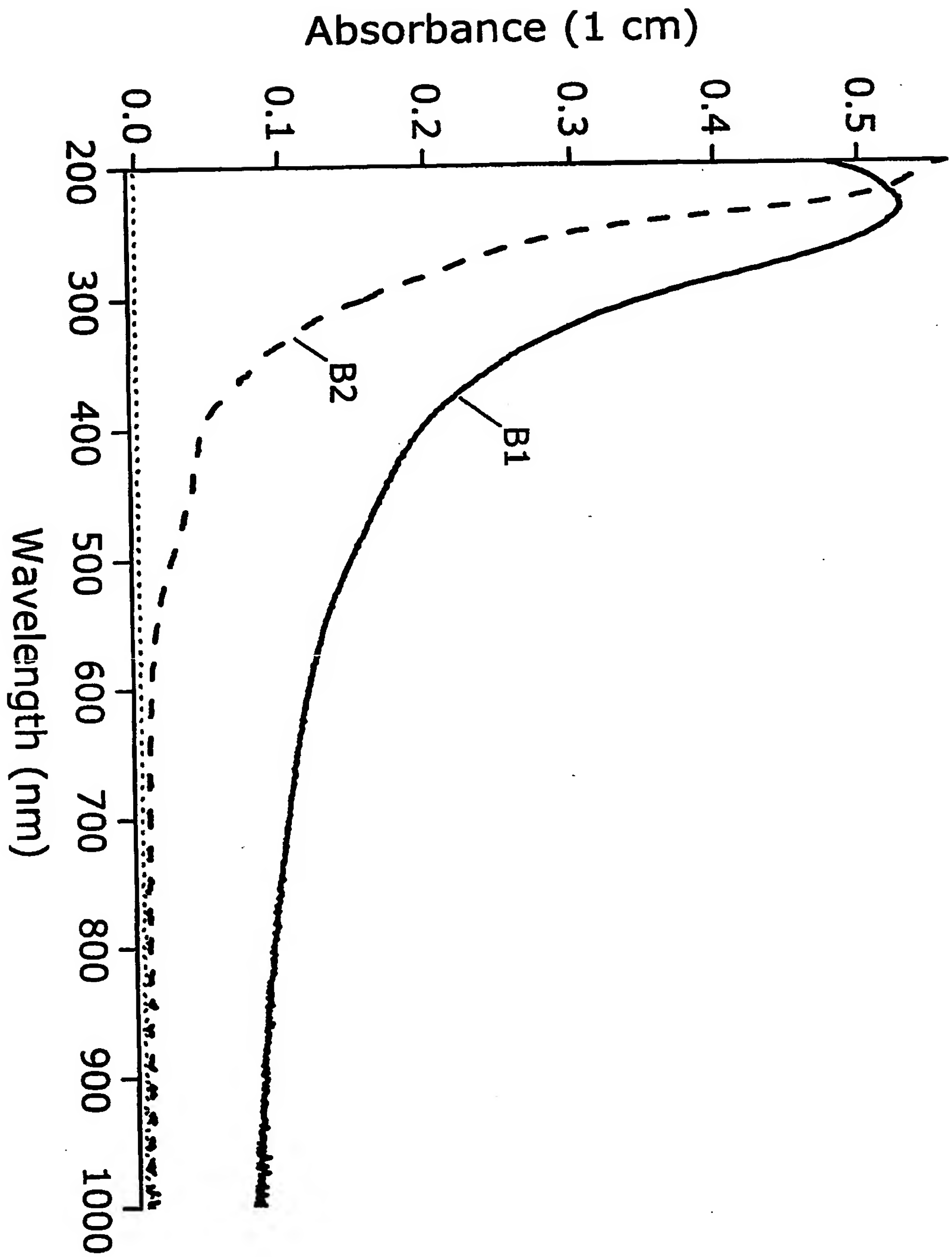
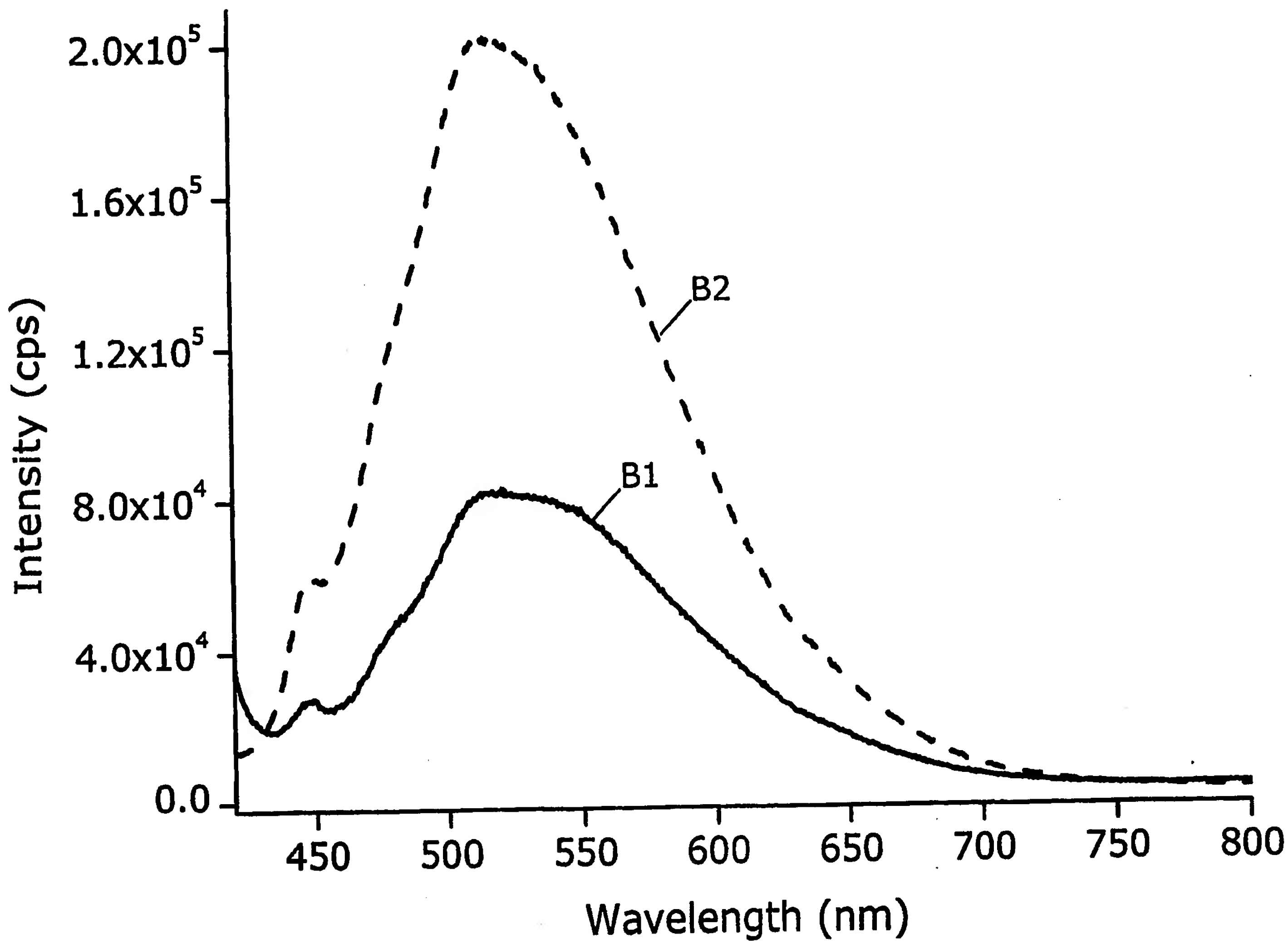
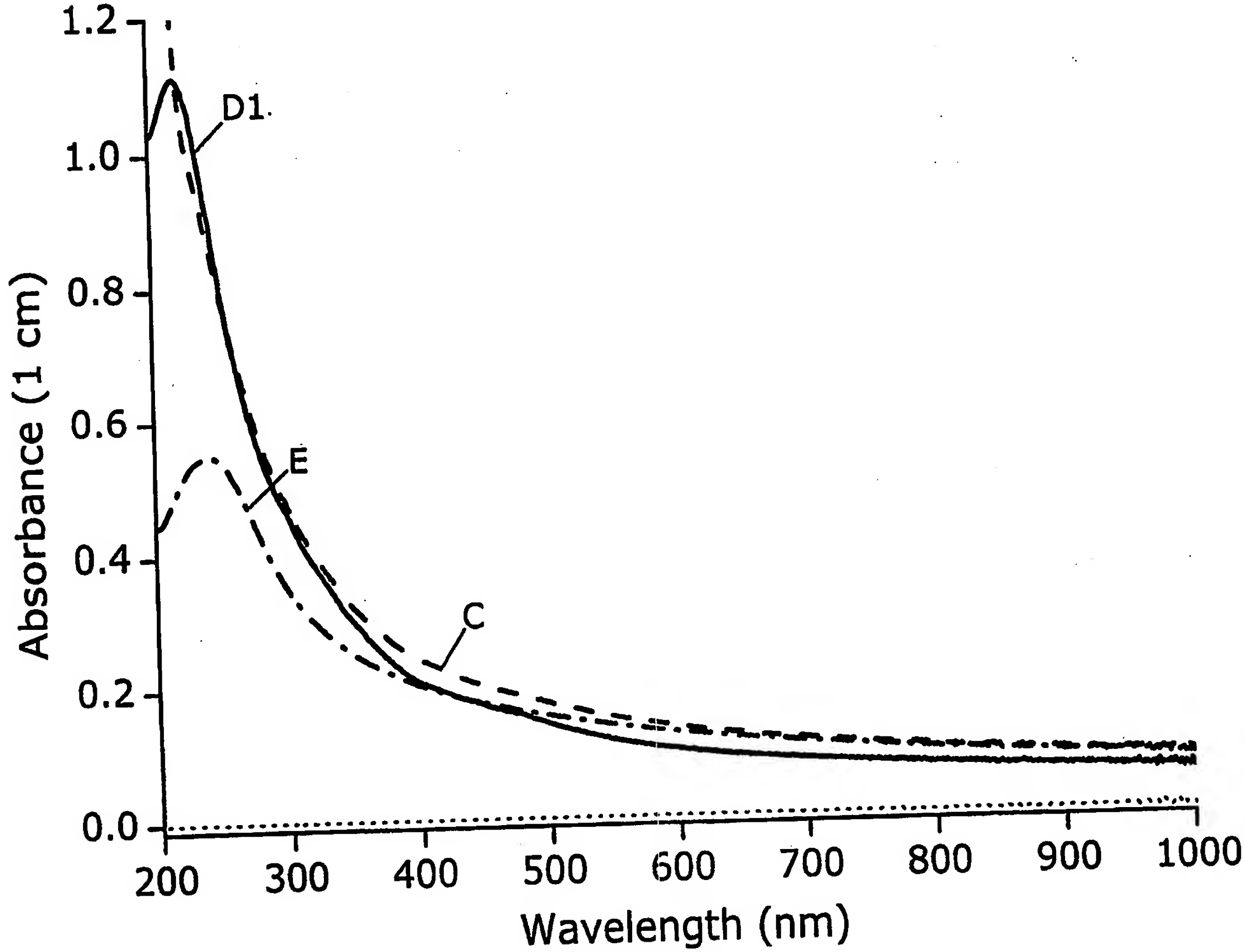

Absorbance (1 cm)
0.0
0.1
0.2
0.3
0.4
0.5
200
300
400
500
600
700
800
900
1000
Wavelength (nm)
B1
B2

Figure 4



Intensity (cps)
2.0x10^5
1.6x10^5
1.2x10^5
8.0x10^4
4.0x10^4
0.0
450
500
550
600
650
700
750
800
Wavelength (nm)
B2
B1

Figure 5



Absorbance (1 cm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
200
300
400
500
600
700
800
900
1000
Wavelength (nm)
D1
E
C

Figure 6

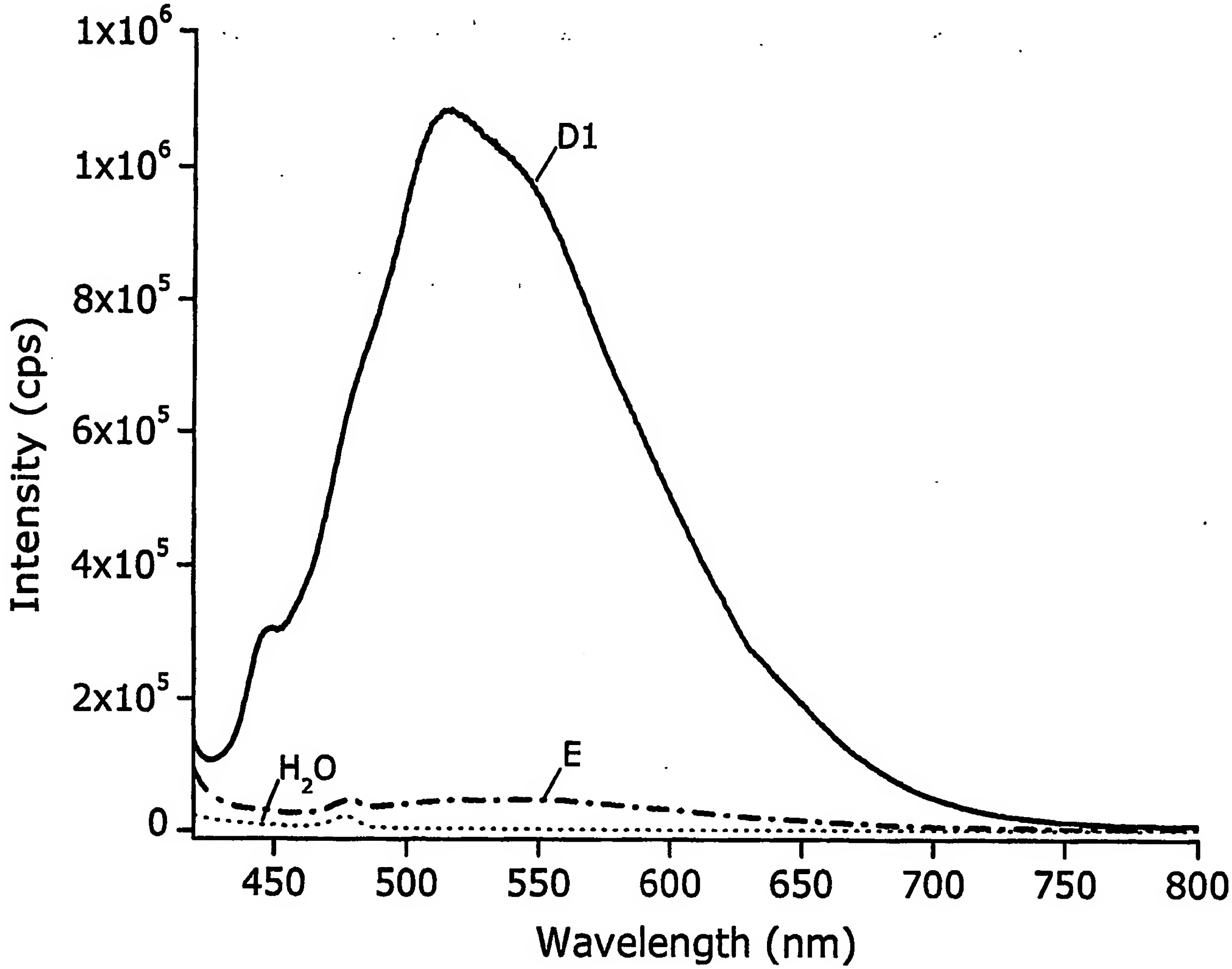

1x10^6
1x10^6
8x10^5
6x10^5
4x10^5
2x10^5
0
Intensity (cps)
450
500
550
600
650
700
750
800
Wavelength (nm)
D1
E
H2O

Figure 7

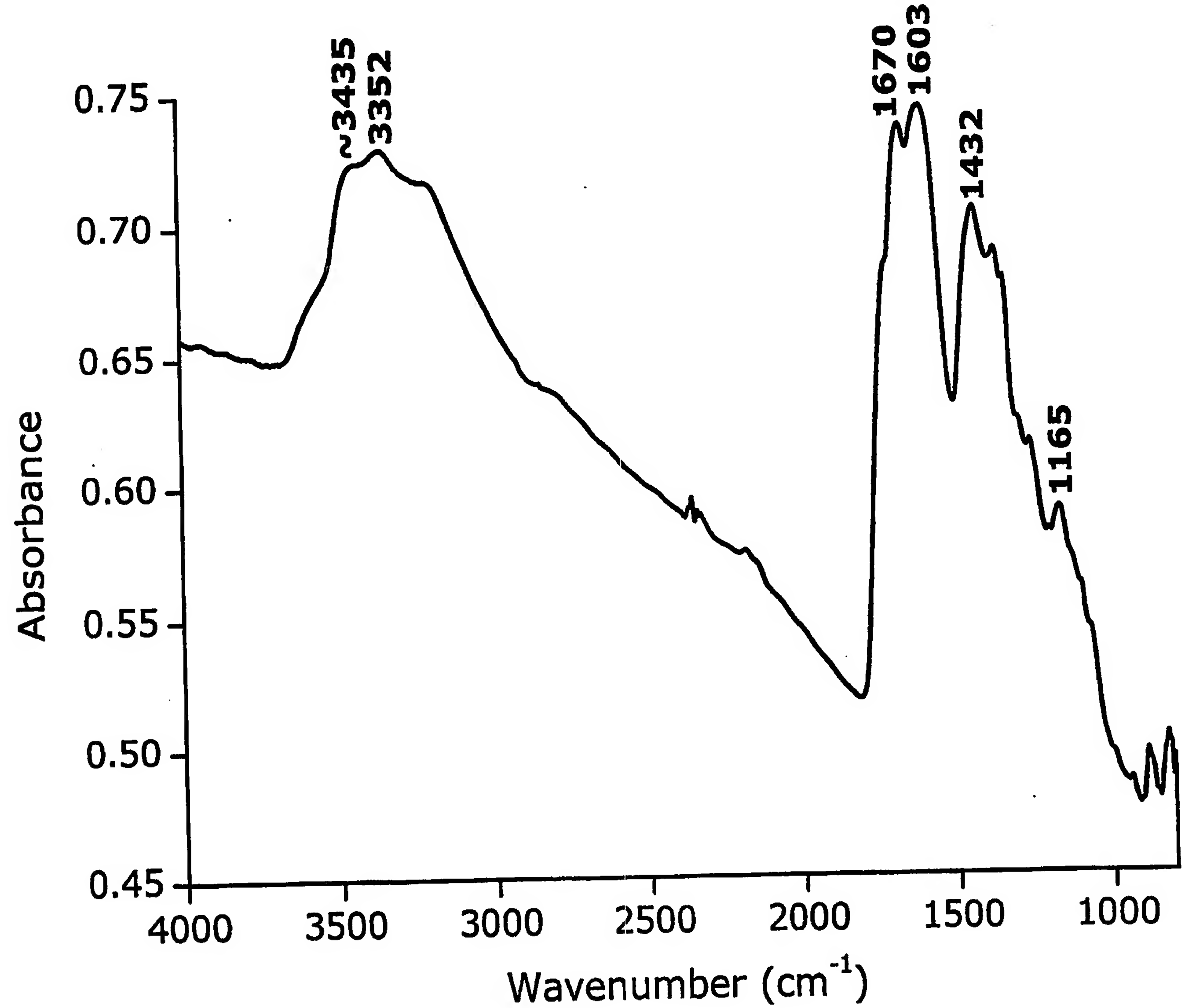

~3435
3352
1670
1603
1432
1165
Absorbance
0.75
0.70
0.65
0.60
0.55
0.50
0.45
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

Figure 8

PCT Application
EP0310600